

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Neil Thomas SIMPKIN BA,

translator to RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages.
3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in German on September 12, 2003 under the number 103 42 600.0 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group Ltd
The 27th day of November 2008

FEDERAL REPUBLIC OF GERMANY

[rubber stamps]



Priority Certificate for the filing of a Patent Application

File Reference: 103 42 600.0

Filing date: 12 September 2003

Applicant/Proprietor: H.C. Stark GmbH,
38642 Goslar/DE

Title: Valve metal oxide powders and process for producing them

IPC: C 01 G 33/00

The attached documents are a correct and accurate reproduction of the original submission for this application.

Munich, 1 July 2004

German Patent and Trademark Office

The President

pp



[signature]

Remus

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Valve metal oxide powders and process for producing them

The invention relates to a process for producing a valve metal oxide powder, in particular an Nb_2O_5 powder or Ta_2O_5 powder, and to valve metal oxide powders obtainable by this process which have a spherical morphology, a mean particle size of from 10 to 80 μm and a high BET surface area.

Valve metals, in particular those belonging to transition groups 4-6 of the periodic system, and of these in particular tantalum and niobium, and alloys thereof, have numerous applications. The valve metals are generally produced by reduction of suitable valve metal compounds, in particular by reduction of valve metal oxides.

However, valve metal oxide powders are of interest not only as a starting material for the production of the corresponding metal powders, but also for numerous further applications. By way of example, niobium and tantalum oxides with high specific surface areas are used in the production of mixed metal oxide materials which are employed, for example, as catalysts and/or functional ceramics.

In order, when producing metal oxide materials of this type, to achieve both intimate mixing of tantalum oxide and/or niobium oxide with the further reactants, such as for example potassium carbonate or molybdenum trioxide, and a reaction sequence which can take place at the lowest possible temperature, it is advantageous to use a spherical morphology of the valve metal oxides in conjunction with a high specific surface area. An overview of niobium-containing catalysts is given by M. Ziolek in "Catalysis Today 78 (2003) 47-64". Niobium oxides, which if possible should have a high specific surface area, are mentioned as the most important class of compounds.

Processes for producing niobium and tantalum oxides with high specific surface areas have already been described in the literature. However, the oxides produced using these processes generally do not have a spherical morphology or are nano-scale valve metal oxide powders.

For example, DE 4 214 724 C2 describes the production of fine ceramic powders with a narrow grain size distribution in a gas phase reaction. Reaction of niobium or tantalum pentachloride with oxygen makes it possible to produce niobium and tantalum pentoxides which, according to the Example, have a specific surface area of 42 m^2/g . However, this process is very complex on account of the gas phase reaction procedure and the release of gaseous chlorine. Moreover, the Nb_2O_5 produced in accordance with the Example contains a total of 700 ppm of metallic impurities.

In "Materials Transactions, Vol. 42, No. 8 (2001), 1623-1628", T. Tsuzuki and P.G. McCormick describe a mechanochemical synthesis of niobium pentoxide nanoparticles. Solid niobium pentachloride together with solid magnesium oxide or sodium carbonate is used to produce Nb_2O_5 with a high specific surface area of 43.3 to 196 m^2/g . However, solid-state reactions only take place very slowly. Reaction times of several hours are described. A further drawback of this process is that the products obtained, on account of the process used, are highly contaminated with sodium. Contaminated niobium pentoxides of this type tend to form $\text{Na}_2\text{Nb}_4\text{O}_{11}$ phases when subjected to a heat treatment ($T > 550^\circ\text{C}$).

Processes for producing mesoporous tantalum oxides are described by J.N. Kondo, Y. Takahara, B. Lee, D. Lu and K. Domen in "Topics in Catalysis Vol. 19, No. 2, 2002, 171-177". Tantalum(V) chloride is hydrolysed by means of moisture which is present in atmospheric air by the addition of the chelating ligand poly(alkylene oxide) block copolymer Pluronic P-123 (BASF) using what is known as the NST (Neutral Surfactant Template) method. The Ta_2O_5 obtained in this way has a very high specific surface area. Drawbacks of this process are firstly the long reaction time of at least 6 days, and also the evolution of HCl gas. Ta_2O_5 with a high specific surface area of 330 to 410 m^2/g is also obtained using what is known as the LAT (Ligand-Assisted Templating) method. According to this method, tantalum(V) ethoxide is hydrolysed with the addition of octadecylamine. However, the product obtained in this way is neither thermally nor mechanically stable and therefore cannot be used for large-scale industrial applications or further processing. Moreover, the tantalum(V) ethoxide used is very expensive.

Nano-scale Nb_2O_5 powders with high specific surface areas can also be produced, in accordance with C. Feldmann and H.-O. Jungk (Angew. Chem. 2001, 113, No. 2, 372-374), by hydrolysis of niobium ethoxide in diethylene glycol. Niobium pentoxides produced in this way have a specific Brunauer-Emmett-Teller (BET) surface area of approximately 100 m^2/g . A further drawback of this process is that the tantalum(V) ethoxide used is very expensive and that it is only possible to obtain nano-scale oxide particles.

In accordance with H. Koninami, K. Oki, M. Kohno, S. Onoue, Y. Kera and B. Ohtani (Journal of Materials Chemistry 2002, 11(2), 604-609), niobium pentoxide with a high specific surface area of 232 m^2/g can also be produced by hydrolysis of niobium butoxide in toluene. Drawbacks of this process are both the possible environmental pollution from the use of toluene as solvent and the high materials cost of the niobium butoxide used.

It is known from German patent application 103 07 716 that spherical niobium and tantalum oxides can be produced by precipitation of heptafluorotantalic acid (H_2TaF_7) or heptafluoroniobic acid (H_2NbF_7) or mixtures thereof from hydrofluoric acid solution by means of bases, in particular

ammonia (NH_3). In this case, tantalic acid $\text{Ta}(\text{OH})_5$ or niobic acid $\text{Nb}(\text{OH})_5$ or a mixture thereof is precipitated and is then converted into the corresponding oxide by heat treatment, known as calcining. However, these oxides have low specific surface areas of from 0.41 to 0.58 cm^2/g .

It is an object of the invention to provide valve metal oxide powders, in particular Nb_2O_5 and
5 Ta_2O_5 powders, which are suitable in particular for solid-state reactions, for example for use as catalyst or for producing catalysts and as electroceramics or for production thereof, and to give a simple process for producing valve metal oxide powders of this type.

The object is achieved by valve metal oxide powders which have a spherical morphology, a D_{50}
value of from 10 to 80 μm and a high BET surface area, and a process for producing them by
10 precipitation of fluoride-containing valve metal compounds with a base at elevated temperature.

Therefore, the subject matter of the invention is a process for producing a valve metal oxide powder by reacting a fluoride-containing valve metal compound with a base in the presence of water and calcining the product which is formed, the reaction taking place at a temperature of from 45°C to the boiling point of the reaction mixture at approx. 105°C.

15 The reaction of a fluoride-containing valve metal compound with a base in the presence of water generally leads to the formation of valve metal hydroxides, for example of niobic acid ($\text{Nb}(\text{OH})_5$) or tantalic acid ($\text{Ta}(\text{OH})_5$). Valve metal hydroxides of this type are insoluble in aqueous systems and are therefore precipitated out of the reaction mixture. This reaction is therefore often referred to as precipitation or a precipitation reaction.

20 According to the invention, the precipitation reaction is carried out at elevated temperature, the temperature preferably being 50 to 75°C, particularly preferably 55 to 70°C.

Although the reaction of the fluoride-containing valve metal compound with the base may be carried out in a batchwise or semi-continuous manner, it is preferable for this precipitation reaction to be carried out continuously. In this preferred embodiment, the procedure is generally for both
25 fluoride-containing valve metal compound and base to be fed continuously to a reaction space and for the product which is formed during the reaction to be taken off continuously.

The water which is required for the reaction can be placed in the reaction space first of all and topped up as required. However, it is most advantageous for the fluoride-containing valve metal compound and the base used each to be used in the form of an aqueous solution or suspension.
30 This means that the water is added together with the reactants, which allows a continuous reaction procedure while ensuring a constant concentration of the reaction partners.

The valve metal is preferably niobium and/or tantalum. Accordingly, the fluoride-containing valve metal compound used is preferably heptafluoroniobic acid (H_2NbF_7) or heptafluorotantalic acid (H_2TaF_7).

5 Depending on the desired purity of the valve metal oxide powder, it may be necessary for the fluoride-containing valve metal compound or the base to be purified, if appropriate more than once, prior to the reaction. In this way, it is possible, if necessary, to reduce the levels of impurities down to the parts per billion (ppb) range.

10 The fluoride-containing valve metal compound is preferably used as an aqueous solution, the concentration of fluoride-containing valve metal compound, based on the valve metal, preferably being 0.3 to 1.2 mol/l, particularly preferably 0.6 to 0.9 mol/l.

The base used is preferably ammonia, alkali metal hydroxide or alkaline-earth metal hydroxide, particularly preferably ammonia. It is very particularly preferable for the base used to be aqueous ammonia solution with an ammonia concentration of from 3 to 15% by weight, preferably from 5 to 10% by weight, particularly preferably from 6 to 10% by weight.

15 The reaction of the fluoride-containing valve metal compound with the base is preferably carried out at a pH, measured at reaction temperature, of from 7 to 14, particularly preferably at a pH, measured at reaction temperature, of from 7.0 to 8.0.

20 During the continuous reaction procedure, the volumetric flows are preferably set in such a way that the ratio of the volumetric flow of aqueous solution of a fluoride-containing valve metal compound to the volumetric flow of aqueous solution of the base is from 1:0.9 to 1:2, preferably from 1:1.0 to 1:1.5. Suitable selection of the volumetric flows and concentrations of the solutions used sets the molar concentration ratio of fluoride-containing valve metal compound, calculated as valve metal, to base to a value of preferably from 1:5.6 to 1:8.5.

25 The absolute volumetric flow of aqueous solution of a fluoride-containing valve metal compound is preferably from 1 to 1 000 l/h, particularly preferably from 200 to 600 l/h.

The residence time of the precipitation product in the reaction space is, for example, between 0.25 and 24 h, but preferably between 30 min and 3 h.

30 The precipitation product obtained in this way, a valve metal hydroxide, is generally separated off by filtration, washed and dried and then calcined to form the valve metal oxide. If necessary, this may be followed by a mechanical processing operation, such as screening, crushing, milling or agglomeration.

The washing of the precipitation product is preferably carried out using deionized water. It is particularly preferable for the washing operation to be carried out in a number of stages, in which case washing is carried out first of all one or more times using the aqueous solution of a base, preferably the base which is also used for precipitation, and then one or more times with deionized water.

The washing is generally followed by a drying step. Drying is preferably carried out at a temperature of from 50-150°C, particularly preferably from 70-110°C. The drying time is preferably 1 to 100 h, particularly preferably 10 to 30 h.

A heat treatment at high temperature, known as calcining, is required in order to convert the precipitation product into the desired valve metal oxide. Calcining is preferably carried out at a temperature of from 250-1 400°C, particularly preferably from 300-600°C. The calcining time is preferably 0.1 to 100 h, particularly preferably 1 to 50 h, especially preferably 1 to 5 h. The calcining is preferably carried out under non-reducing conditions, for example in the presence of noble gas or atmospheric air, preferably in the presence of atmospheric oxygen.

The structure of the valve metal oxide particles can be stabilized by a high-temperature treatment, preferably in the temperature range of $> 1\ 000^{\circ}\text{C}$, particularly preferably close to the melting point of the oxides. This makes it possible to reinforce sintered bridges between the primary grains and to deliberately vary the pore structure.

After any high-temperature treatment has taken place, it is once again possible to carry out a mechanical processing operation, such as screening, crushing or milling. Any impurities which may be introduced, such as carbon, can be removed by subsequent calcining in air, preferably at temperatures of between 800-1 200°C.

The process according to the invention makes it possible to produce spherical valve metal oxide powders having a mean particle diameter D_{50} , determined by means of MasterSizer in accordance with ASTM B 822, of 10 to 80 μm , preferably between 15 and 40 μm , and a high BET surface area, determined by means of the N_2 3-point method in accordance with ASTM D 3663, of at least 10 m^2/g .

Furthermore, the valve metal oxide powders obtained are distinguished by a very narrow grain size distribution of the spherical agglomerates. Valve metal oxides produced in accordance with the invention can be converted by reduction into valve metal powders or valve metal suboxides which have similar surface areas and capacitances to the known, high-capacitance powders. Unlike the latter, the free-flowing properties are retained. Therefore, powders of this type are eminently

suitable for the production of capacitor anodes and capacitors. On account of the homogenous grain size distribution and relatively low agglomerate size, a uniform packing density in the anode and therefore an improvement in the quality and yield for the user are achieved. Furthermore, it is also possible for the secondary structure to be set in such a way that good impregnability of the agglomerate is retained even with a very fine primary structure.

Therefore, the subject matter of the invention is also spherical valve metal oxide powders having a mean particle diameter D_{50} , determined by means of MasterSizer in accordance with ASTM B 822, of from 10 to 80 μm , and a BET surface area, determined by means of the N_2 3-point method in accordance with ASTM D 3663, of at least 10 m^2/g .

10 Valve metal oxide powders of this type are obtainable by the process according to the invention.

Imaging methods are used to determine the morphology of the valve metal oxide powders. A two-dimensional image of a powder specimen is obtained using a scanning electron microscope with 200 \times magnification. For this purpose, the powder is applied to a square specimen slide with a sticky surface. A viewing area in which at least 200 particles are visible is examined. The powder particles which are visible in this image are analysed. For this purpose, a circle which touches the two points on the particle periphery which are at the maximum distance apart is drawn around an imaged powder particle. A further circle which has an identical centre and in this case touches the two points on the particle periphery which are at the minimum distance apart is drawn. The ratio of the diameters of these two circles is used as a criterion for describing the morphology of the valve metal oxide powder. An ideally spherical powder particle has a ratio of 1, since all the points on the surface of the powder particle are at the same distance from the centre of the particle.

The term spherical valve metal oxide powders, i.e. valve metal oxide powders whose powder particles are approximately spherical in form, are to be understood as meaning powders in which at least 95% of the powder particles have a ratio of the diameter of the larger circle to the diameter of the smaller circle of from 1.0 to 1.4.

The mean particle diameter D_{50} , determined by means of MasterSizer in accordance with ASTM B 822, is preferably from 15 to 40 μm .

The BET surface area determined by means of N_2 3-point method in accordance with ASTM D 3663 is preferably at least 20 m^2/g , particularly preferably at least 40 m^2/g , particularly preferably at least 60 m^2/g . The maximum BET surface area is preferably 225 m^2/g .

The valve metal oxide powders according to the invention are preferably niobium or tantalum oxide powders, for example NbO_2 , NbO , Nb_2O_5 , TaO_2 , TaO , Ta_2O_5 powders or a niobium or tantalum suboxide, particularly preferably Nb_2O_5 or Ta_2O_5 powders.

5 The invention is explained in more detail below on the basis of examples; the examples are intended to make it easier to understand the principle of the invention and are not intended to be understood as constituting any restriction on the scope of the invention.

Examples

The metal oxide powders or metal powders produced in the following examples were analysed for various chemical and physical properties as indicated in the Examples. Unless stated otherwise, the procedure was as follows:

- 5 The grain size distribution (D_{10} , D_{50} and D_{90} values) was determined by means of laser diffraction using a MasterSizer S μ produced by MALVERN (ASTM B 822) and the specific surface area was determined using the known Brunauer, Emmett and Teller method (BET method) by means of the N_2 3-point method in accordance with ASTM D 3663. Unless indicated otherwise, the percentages are percentages by weight.

10 Comparative Example 1

Nb_2O_5 with a high specific surface area

- 80 ml of deionized water were added to 200 ml of niobium(V) ethoxide with stirring. The niobium(V) hydroxide (niobic acid) obtained in this way was filtered off via a suction filter and washed with deionized water. Then, the niobium(V) hydroxide was dried for 17 hours at 100°C and then calcined in air for 4 hours at 500°C. 280 g of Nb_2O_5 with a specific surface area of 80 m²/g were obtained.
- 15

Fig. 1 shows a scanning electron microscope image of the Nb_2O_5 produced in this way under 100 × magnification. It is clearly apparent that the individual powder particles are irregularly shaped and are in some cases in platelet form.

20 Comparative Example 2

Spherical Nb_2O_5 with a low specific surface area

- With an initial charge of 200 l of deionized water, 7490 l of aqueous H_2NbF_7 solution (Nb concentration: 80 g/l) were continuously precipitated with 7500 l of 9% strength aqueous NH_3 solution. The temperature of the solution was approx. 32°C, and the pH was set to 7.6 ± 0.4 . The suspension obtained in this way was forced through a pressure nutsche, then washed with 3% strength aqueous NH_3 solution and then with deionized water. The moist niobium(V) hydroxide obtained was dried for 24 h at 100°C in a drying cabinet. An Nb_2O_5 powder with a specific surface area of 1.6 m²/g was obtained by calcining the dried niobium(V) hydroxide in air at a temperature of 400°C for 2 h.
- 25

Comparative Example 3

Ta₂O₅ with a high specific surface area

- 5 A stoichiometric excess of deionized water was added to 1000 ml of tantalum(V) ethoxide with stirring. The tantalum(V) hydroxide obtained in this way was filtered off via a suction filter and washed with deionized water. Then, the tantalum(V) hydroxide was dried for 17 h at 75°C. 872.1 g of tantalum(V) hydroxide with a residual water content of 9.78% was obtained. 55 g of this material was calcined in air for 2 hours at 500°C. The Ta₂O₅ obtained in this way had a specific surface area of 76 m²/g.

Comparative Example 4

- 10 Spherical Ta₂O₅ with a low specific surface area

- With an initial charge of 300 l of deionized water, 6 360 l of aqueous H₂TaF₇ solution with a concentration of approx. 82 g/l of Ta were continuously precipitated with 5655 l of 6% strength aqueous NH₃ solution, such that the pH was 7.6 ± 0.4. The temperature of the solution was approx. 35°C. The suspension obtained in this way was pressed through a pressure nutsche, then washed
15 firstly with a 3% strength aqueous NH₃ solution and then with deionized water. The moist tantalum(v) hydroxide obtained was dried for 24 h at 100°C in a drying cabinet and then calcined in air for 2 hours at 400°C. The Ta₂O₅ produced in this way had a specific surface area of 1 m²/g.

Example 1

- 20 With an initial charge of 300 l of deionized water, 3 700 l of aqueous H₂NbF₇ solution with a concentration of 84 g/l of Nb were precipitated continuously with 5 500 l of 6% strength aqueous NH₃ solution. The aqueous H₂NbF₇ solution was added with a volumetric flow of 300 l/h, and the 6% strength aqueous NH₃ solution was added with a volumetric flow of 450 l/h. The pH was set to 7.6 ± 0.4. The temperature of the solution was 56°C. The suspension obtained in this way was filtered off via a pressure nutsche, washed with 3% strength aqueous NH₃ solution and then with
25 deionized water. The moist niobium(V) hydroxide was dried for 24 h at 100°C in the drying cabinet. Calcining of the dried niobium(V) hydroxide at a temperature of 500°C for 2 h resulted in an Nb₂O₅ powder which had a specific surface area of 94 m²/g and a spherical morphology.

MasterSizer – Analysis values [μm]:	D10	1.77
	D50	17.26
	D90	33.27

Example 2

5 With an initial charge of 400 l of deionized water, 4 662 l of aqueous H_2NbF_7 solution with a concentration of 81 g/l of Nb were precipitated continuously with 4 600 l of 9% strength aqueous NH_3 solution. The aqueous H_2NbF_7 solution was added with a volumetric flow of 300 l/h, and the 9% strength aqueous NH_3 solution was added with a volumetric flow of 300 l/h. The pH was set to 7.6 ± 0.4 . The temperature of the solution was 63°C . The suspension obtained in this way was
10 filtered off via a pressure nutsche, washed with 3% strength aqueous NH_3 solution and then with deionized water. The moist niobium(V) hydroxide obtained was dried for 24 h at 100°C in a drying cabinet. The niobium(V) hydroxide had a specific surface area of $201 \text{ m}^2/\text{g}$ and a mainly spherical morphology. Calcining for 2 h at a temperature of 500°C resulted in an Nb_2O_5 powder with a specific surface area of $116 \text{ m}^2/\text{g}$ and a spherical morphology.

15	MasterSizer – Analysis values [μm]:	D10	2.10
		D50	20.21
		D90	37.28

Fig. 2 shows a scanning electron microscope (SEM) image of the Nb_2O_5 powder obtained ($100\times$ magnification). The spherical morphology is clearly apparent.

20. Example 3

With an initial charge of 400 l of deionized water, 9 020 l of aqueous H_2NbF_7 solution with a concentration of 80 g/l Nb were continuously precipitated with 10 000 l of 9% strength aqueous NH_3 solution. The aqueous H_2NbF_7 solution was added with a volumetric flow of 300 l/h and the 9% strength aqueous NH_3 solution was added with a volumetric flow of 300 l/h. The pH was set to 7.6 ± 0.4 . The temperature of the solution was 69°C . The suspension obtained in this way was filtered off via a pressure nutsche, washed with 3% strength aqueous NH_3 solution and then with deionized water. The moist niobium(V) hydroxide obtained was dried for 24 h at 100°C in a drying cabinet. Calcining for 2 h at a temperature of 400°C resulted in Nb_2O_5 powder with a specific surface area of $140 \text{ m}^2/\text{g}$ and a spherical morphology.

MasterSizer- Analysis values [μm]:	D10	2.60
	D50	20.97
	D90	38.12

Fig. 3 shows a scanning electron microscope (SEM) image of the Nb_2O_5 powder obtained (200 ×
5 magnification). The spherical morphology is clearly apparent.

Patent Claims:

1. Process for producing a valve metal oxide powder by reacting a fluoride-containing valve metal compound with a base in the presence of water and calcining the product which is formed, characterized in that the reaction takes place at a temperature of at least 45°C.
- 5 2. Process according to Claim 1, characterized in that the reaction of the fluoride-containing valve metal compound with the base takes place continuously.
3. Process according to Claim 1 or 2, characterized in that the fluoride-containing valve metal compound and the base which is used are each used in the form of an aqueous solution or suspension.
- 10 4. Process according to any of Claims 1 to 3, characterized in that the fluoride-containing valve metal compound is H_2NbF_7 or H_2TaF_7 .
5. Process according to any of Claims 1 to 4, characterized in that the base used is ammonia, alkali metal hydroxide or alkaline-earth metal hydroxide.
- 15 6. Process according to Claim 5, characterized in that the base used is aqueous ammonia solution with an ammonia concentration of from 3 to 15% by weight.
7. Process according to any of Claims 1 to 6, characterized in that the reaction of the fluoride-containing valve metal compound with the base is carried out at a pH, measured at reaction temperature, of from 7 to 14.
- 20 8. Spherical valve metal oxide powder having a mean particle diameter D_{50} , determined by means of MasterSizer in accordance with ASTM B 822 of from 10 to 80 μm , characterized in that the BET surface area, determined by means of N_2 3-point method in accordance with ASTM D 3663, is at least 10 m^2/g .
9. Valve metal oxide powder according to Claim 8, characterized in that the valve metal oxide is a niobium oxide or tantalum oxide.
- 25 10. Valve metal oxide powder according to Claim 9, characterized in that the valve metal oxide is Nb_2O_5 or Ta_2O_5 .

Valve metal oxide powder and process for producing it

Abstract

Process for producing a valve metal oxide powder, in particular an Nb_2O_5 powder or Ta_2O_5 powder, by reacting a fluoride-containing valve metal compound with a base in the presence of water and calcining the product which is formed, the reaction taking place at a temperature of at least 45°C , and valve metal oxide powders obtainable by this process which have a spherical morphology, a D_{50} value of from 10 to 80 μm and a high BET surface area.

Publish with Fig. 2

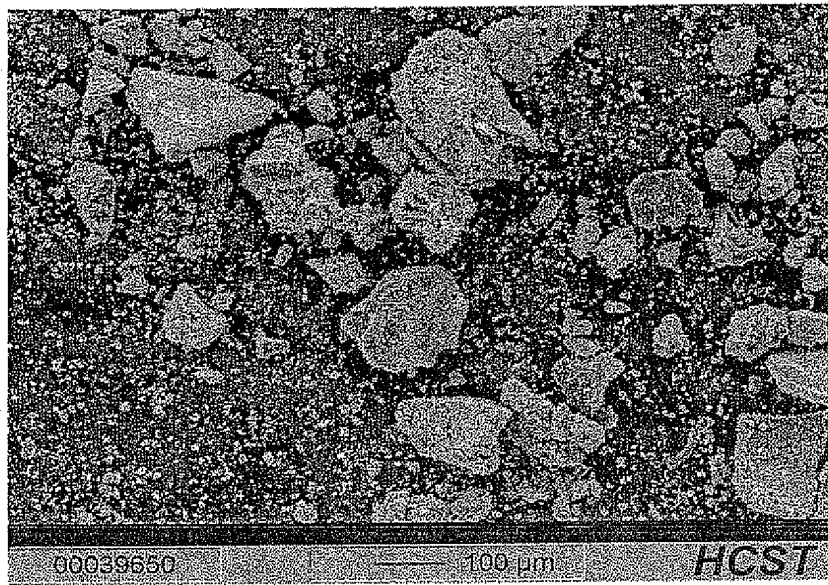


Fig. 1

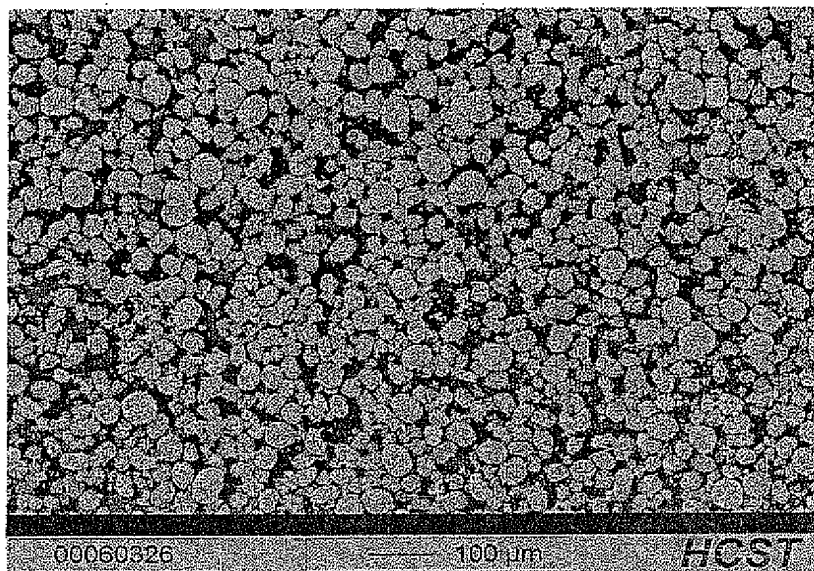


Fig. 2

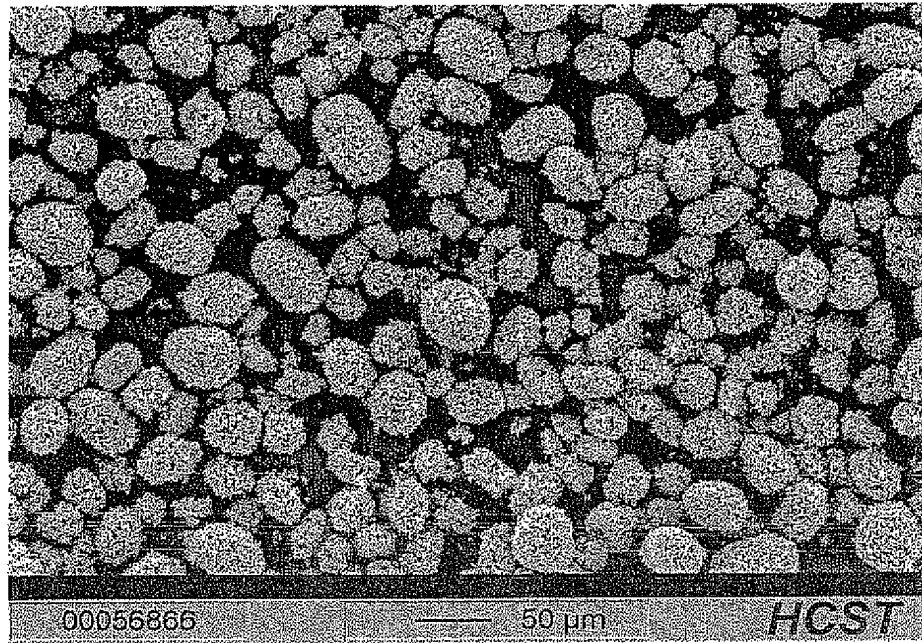


Fig. 3